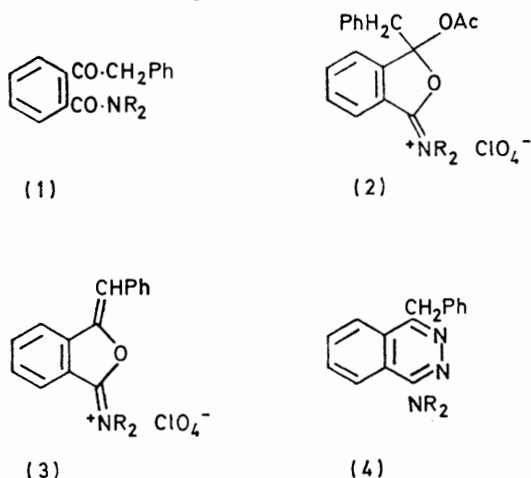


Synthesis and Transformations of Phthalanylideneammonium Salts

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Several phthalanylideneammonium perchlorates have been prepared by the action of acetic anhydride and perchloric acid on *NN*-disubstituted *o*-acylbenzamides. 3-Benzylidenephthalan-1-ylidenedimethylammonium perchlorate (3a) reacts with hydrazine, methylhydrazine, and phenylhydrazine to give derivatives of phthalazine, and with benzylamine in acetic acid to yield the hydroperchlorate of an isoindoline. Treatment with ethanolic benzylamine results in rearrangement to give 3-benzylamino-2-phenylinden-1-one; analogous compounds are formed by reaction with ammonia, aniline, dimethylamine, and methanolic triethylamine. Ethyl cyanoacetate and cyanoacetamide similarly yield derivatives of 2-phenylindan-1-one. Cyclisation of *o*-isobutyryl-*NN*-dimethylbenzamide gives 3-acetoxy-3-isopropylphthalan-1-ylidenedimethylammonium perchlorate (23) which has been converted into the isopropylidene analogue (25a) of compound (3a). The preparation of the corresponding diphenylmethylene perchlorate (25b) is also reported. The latter two salts react with ethyl cyanoacetate without rearrangement to yield derivatives of 1,3-dimethylenephthalan.

In the course of our work¹ on the cyclisation of compounds of the general formula $-\text{OC}\cdot\text{X}\cdot\text{Y}\cdot\text{CO}-$, we have examined the action of acetic anhydride-perchloric acid on *NN*-disubstituted *o*-acylbenzamides, $\text{>N}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}<$, and obtained 3-methylenephthalan-1-ylideneammonium perchlorates. This paper describes the synthesis and chemistry of several representatives of this novel class of heterocyclic cation.



a; R = Me
b; R₂ = C₄H₈O

The required *o*-acylbenzamides were readily prepared by the action of secondary amines on 3-methylenephthalides; thus, benzylidenephthalide and dimethyl-

¹ G. V. Boyd and P. H. Wright, *J.C.S. Perkin I*, 1972, 1140, and references cited therein.

amine gave the dimethylamide (1a);² and morpholine formed the morpholide (1b). The dimethylamide (1a) reacted with acetic anhydride and perchloric acid to yield an unstable hygroscopic perchlorate whose i.r. spectrum (ν_{max} 1775 cm⁻¹) indicated the presence of the acetoxy-compound (2a). When the crude perchlorate was heated in acetic acid it was converted into the pale yellow benzylidene salt (3a).³ The salt absorbs at 1685 cm⁻¹ (C=N⁺) and its n.m.r. spectrum shows non-equivalence of the *N*-methyl groups. The constitution of the salt was confirmed by aqueous hydrolysis, which gave benzylidenephthalide.

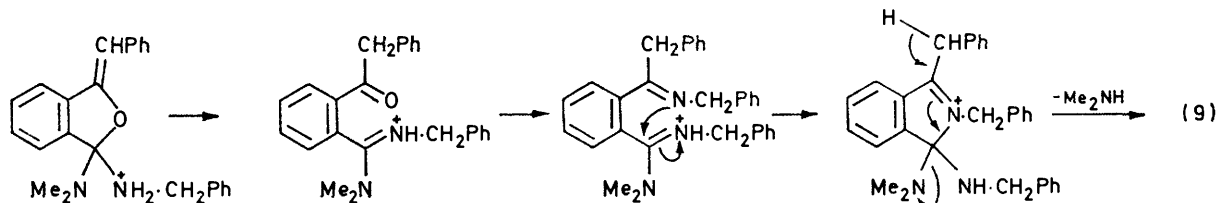
The perchlorate (3a) is stable and not hygroscopic. It reacts readily with nucleophiles to yield a variety of products formed by ring-opening and subsequent re-cyclisation. Derivatives of phthalazine are obtained by reaction with hydrazines: hydrazine itself gave 1-benzyl-4-dimethylaminophthalazine (4a), while methylhydrazine gave the phthalazinone (5), identical with a sample prepared⁴ by methylation of 4-benzylphthalazin-1(2*H*)-one in alkaline solution. The action of phenylhydrazine on the perchlorate was more complex, affording the orange phenylhydrazonodihydrophthalazine (6); this compound showed weak NH absorption in its i.r. and a methylene signal in its n.m.r. spectrum. The formation of the various products can be rationalised (Scheme 1) by assuming initial attack at C-1 of the phthalan ring, followed by ring-opening and proton transfer. The resulting ketonic intermediates in the reactions with

² M. Sekiya and Y. Terao, *Yakugaku Zasshi*, 1968, **88**, 1085.

³ For a preliminary account of the chemistry of this salt, see G. V. Boyd, *Tetrahedron Letters*, 1972, 2711.

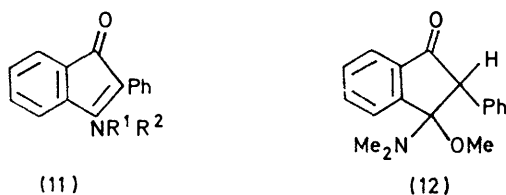
⁴ O. Bromberg, *Ber.*, 1896, **29**, 1434.

amine the tertiary enamine (11d). We suggest that the formation of these indenones proceeds *via* the cross-conjugated 1,5-dipoles shown in Scheme 3. The dimethylamino-compound (11d) was produced quantitatively when the benzylidene salt (3a) was treated with methanolic triethylamine; the reaction is thought to occur by attack of methoxide anion, rearrangement to the indanone (12), and elimination of methanol.



SCHEME 2

Treatment of the salt (3a) with ethyl cyanoacetate in the presence of triethylamine gave a bluish purple solution from which hydrochloric acid precipitated a colourless compound, $C_{20}H_{15}NO_3$, in high yield. The n.m.r. spectrum of this product was consistent with either structure (13) or (14), but the i.r. spectrum in Nujol or chloroform appeared to favour the phthalan structure (13) since



- (11)
 a; $R^1 = PhCH_2, R^2 = H$
 b; $R^1 = R^2 = H$
 c; $R^1 = Ph, R^2 = H$
 d; $R^1 = R^2 = Me$

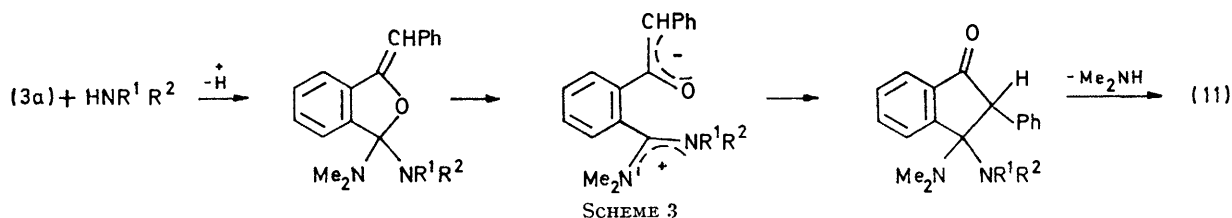
only one band was observed in the carbonyl region. The compound dissolved in alkali or aqueous amines with an intense mauve colour (λ_{max} 540 nm) and was regenerated

structure (16), is ruled out by a strong nitrile peak in the i.r. spectrum, characteristic of $\alpha\beta$ -unsaturation, and by its electronic spectrum, which contained no band beyond 332 nm, whereas the model methylphenylindenone (17) absorbs maximally at 420 nm.⁸ The analogue (18) was prepared by the action of cyanoacetamide and triethylamine on the phthalanylidene salt (3a). The i.r. spectrum of this keto-amide was unexceptional and its

electronic spectrum virtually the same as that of the previous compound; the derived anions likewise absorb at the same wavelengths. The indenones are thought to be formed *via* the intermediates (19) and (20); the latter is closely related to the anion (21) which is involved⁹ in the well-known sodium methoxide-induced rearrangement of benzylidenephthalide to 2-phenylindane-1,3-dione.¹⁰

The morpholine analogue (3b) of the salt was prepared by cyclisation of the morpholide (1b) and treatment of the salt (3b) with hydrazine gave the phthalazine (4b).

The synthesis of more highly substituted phthalanylideneammonium salts was investigated next. The amide (22a), formed by the action of dimethylamine on isopropylidenephthalide, reacted with acetic anhydride-perchloric acid to give a high yield of an iminium perchlorate which proved to be the acetate (23), an analogue of the suspected intermediate (2a). The i.r. spectrum of the new salt (23) exhibited bands at 1770 (ester) and 1690 ($C=N^+$) cm^{-1} and its n.m.r. spectrum showed the presence of the isopropyl substituent whose methyl groups are magnetically non-equivalent. The acetoxy-compound (23) on treatment with hydrazine eliminated acetic acid



SCHEME 3

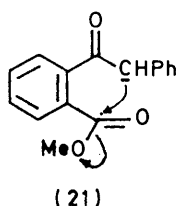
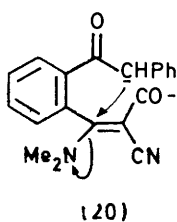
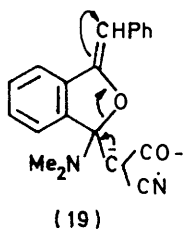
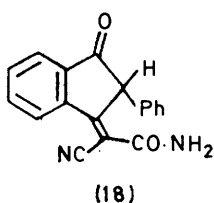
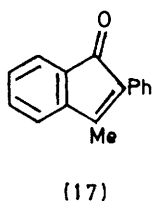
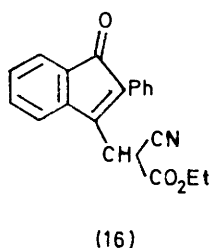
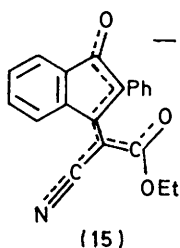
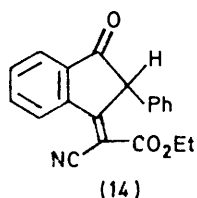
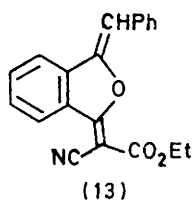
on acidification. The anion most reasonably has the extensively conjugated structure (15) and, while it is conceivable that the phthalan (13) rearranges to this anion on treatment with base, the reverse change is difficult to envisage. It was therefore concluded that the compound is the indanone (14), with coincident ester and ketone carbonyl absorptions; this assignment was supported by the preparation of the 2,4-dinitrophenylhydrazone. The remaining alternative, the tautomeric

to form the phthalazine (24). When the acetoxy-perchlorate (23) was heated in acetic acid or in acetic anhydride it was transformed into the isopropylidene compound (25a), whose n.m.r. spectrum showed that the *N*- as well as the *C*-methyl groups are non-equivalent. The salt (25a) is stable and not hygroscopic; it could not

⁹ S. L. Shapiro, K. Geiger, and L. Freedman, *J. Org. Chem.*, 1960, **25**, 1860.

¹⁰ F. Nathanson, *Ber.*, 1893, **26**, 2576.

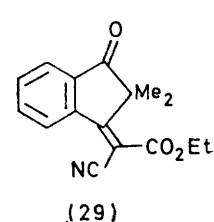
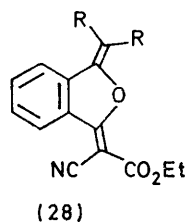
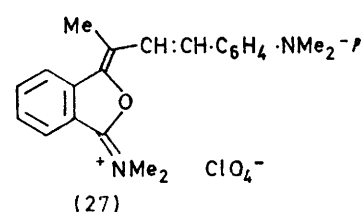
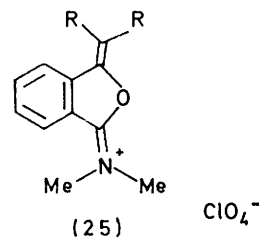
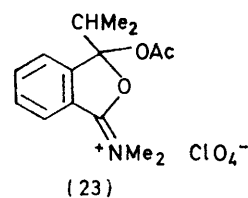
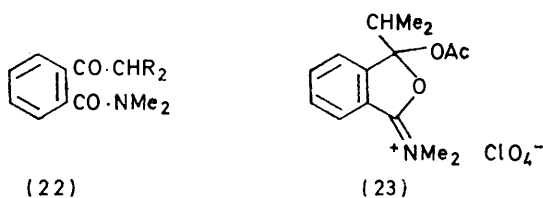
be deprotonated. Experiments to demonstrate the formation of its conjugate base (26) were unsuccessful.



No adducts derived from (26) were obtained when the perchlorate (25a) was treated with *N*-phenylmaleimide or dimethyl acetylenedicarboxylate in the presence of 1,8-bis(dimethylamino)naphthalene¹¹ as a proton abstractor and the salt did not react with *p*-dimethylaminobenzaldehyde; formation of the hoped-for condensation product (27) would have implicated the intermediacy of the isobenzofuran [see arrows in formula (26)].

Intractable oils were produced when the isopropylidene salt (25a) was treated with ethanolic solutions of benzylamine, aniline, dimethylamine, dibenzylamine, mor-

pholine, or triethylamine; but the salt reacted readily with ethyl cyanoacetate in the presence of triethylamine to give a crystalline yellow ester, which, like compound (14), exhibited only one band in the carbonyl region. Since it absorbed at a considerably longer wavelength (390 nm) than the latter it must contain a more conjugated system and it was therefore considered to be the phthalan (28a) rather than the dimethyl analogue (29) of the indanone (14). This assignment was supported by the failure of the compound to yield a 2,4-dinitrophenylhydrazone, and by the n.m.r. spectrum of its solution in benzene, which showed two signals for the two methyl groups. Treatment of 3-(diphenylmethylene)phthalide with dimethylamine gave the amide (22b), which was converted into the diphenylmethylenephthalanyliden ammonium perchlorate (25b). The n.m.r. spectrum of this salt is noteworthy as each of the two *N*-methyl signals is split into a doublet. Models of the cations (25a) and (25b) indicate that in the former both *C*-methyl



a; R = Me
b; R = Ph

groups can lie in the central plane of the molecule but in the latter the phenyl groups are severely twisted out of this plane. In neither cation can the *N*-methyl groups

¹¹ R. W. Alder, P. S. Bowman, W. R. S. Steele, and D. R. Winterman, *Chem. Comm.*, 1968, 723.

attain coplanarity with the phthalan system. The isopropylidene salt consequently exists in only one conformation, with one *N*-methyl group above the plane of the rest of the molecule and the other below it, whereas the diphenyl compound exists in two conformations: in the first, the phenyl and *N*-methyl substituents adjacent to the benzene ring are both above the central plane, and in the second, one is above and the other below. This would account for the two *N*-methyl singlets in the spectrum of compound (25a) and for the splitting of each of these signals in the spectrum of the other salt (25b).

The diphenylmethylene perchlorate (25b) reacted with ethyl cyanoacetate to yield a bright yellow compound, which is assigned structure (28b) since it absorbs at an even longer wavelength than does the dimethyl analogue (28a). The observation that the perchlorates (25a) and (25b) yield phthalans rather than indanones in the reaction with ethyl cyanoacetate is related to the failure of the corresponding phthalides to rearrange to indanediones in the presence of sodium methoxide: isopropylidene-phthalide gives a mixture of 3-isopropyl-3-methoxyphthalide and methyl *o*-isobutyrylbenzoate¹² while diphenylmethylene-phthalide yields sodium *o*-(diphenylacetyl)benzoate, together with an anomalous product, 1,1,2,2-tetraphenylethane.¹³

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra refer to Nujol mulls unless stated otherwise; ¹H n.m.r. spectra were measured at 60 MHz with a Perkin-Elmer R 10 instrument. U.v. spectra were measured for ethanolic solutions. Perchloric acid was of 70%, and ethanolic dimethylamine of 33% strength. Light petroleum refers to the fraction with b.p. 40–60°.

NN-Dimethyl-*o*-(phenylacetyl)benzamide (1a).—3-Benzylidene-phthalide (66.6 g) was added to ethanolic dimethylamine (130 ml), and the resulting solution, when kept at 0° overnight, deposited the product (1a) (73.8 g, 92.6%), m.p. 103–104° (lit.,² 103–104°), ν_{\max} 1690 and 1625 cm⁻¹ (Found: C, 76.8; H, 6.5; N, 5.2. Calc. for C₁₇H₁₇NO₂: C, 76.4; H, 6.4; N, 5.25%).

N-[*o*-(Phenylacetyl)benzoyl]morpholine (1b).—A mixture of 3-benzylidene-phthalide (22.2 g), morpholine (17 ml), and ethanol (30 ml) was briefly heated on the steam-bath and then set aside for 12 h. Addition of water gave an oil which solidified to give the *morpholide* (1b) (28.6 g, 92.6%), m.p. 103° (from ethanol), ν_{\max} 1690, 1630, and 1110 cm⁻¹ (Found: C, 73.7; H, 6.2; N, 4.45. C₁₉H₁₉NO₃ requires C, 73.75; H, 6.2; N, 4.55%).

Cyclisation of the Dimethylamide (1a).—The amide (54.6 g) was suspended in acetic anhydride (140 ml) and perchloric acid (25 ml) was slowly added at such a rate that the temperature did not rise above 70°. The resulting solution was cooled and ether was added to precipitate a viscous oil which was repeatedly washed with ether. A small portion was stirred with acetic acid, whereupon it solidified. The solid, after being washed with ether, had ν_{\max} 1775 cm⁻¹. The remainder of the oil was dissolved in acetic acid (140 ml) and the solution was heated to boiling; crystals soon

appeared. Heating was continued for 30 min and the mixture was then cooled. The crude product (58.2 g, 83.4%) was collected and washed with ether; it had m.p. 231° (with previous softening). (3-Benzylidene-phthalan-1-ylidene)dimethylammonium perchlorate (3a) separated from acetonitrile in pale yellow rectangular prisms, m.p. 249–250.5°, ν_{\max} 1685, 1600, and 1060br cm⁻¹, τ (CF₃·CO₂H) 1.7–2.62 (m, Ar), 3.03 (s, =CH), 6.02 (s, NMe), and 6.15 (s, NMe) (Found: C, 58.3; H, 4.5; N, 4.0. C₁₇H₁₆ClNO₅ requires C, 58.4; H, 4.6; N, 4.0%). A solution of the foregoing salt (175 mg) in acetonitrile (5 ml) and *N*-hydrochloric acid (8 ml) was heated under reflux for 3 h. The solvents were removed and the residue was recrystallised from ethanol, giving 3-benzylidene-phthalide (90 mg, 81%), m.p. 99°, identified by direct comparison with an authentic specimen.

Reaction of the Perchlorate (3a) with Hydrazine and its Derivatives.—(a) The salt (3a) (1.75 g) was added to a solution of hydrazine hydrate (0.38 g) and triethylamine (0.75 g) in ethanol (6 ml). The resulting solution was kept for 1 h and then treated with water (5 ml). 1-Benzyl-4-dimethylaminophthalazine (4a) (1.19 g, 91%) separated as an oil which rapidly solidified; m.p. 129.5–130.5° (from aqueous ethanol), ν_{\max} 1610 cm⁻¹, τ (CDCl₃) 1.87–2.92 (m, Ar), 5.42 (s, CH₂), and 6.84 (s, 2 × NMe) (Found: C, 77.4; H, 6.6; N, 16.2. C₁₇H₁₇N₃ requires C, 77.5; H, 6.5; N, 16.0%).

(b) Addition of the perchlorate (3a) (1.75 g) to a solution of methylhydrazine (0.46 g) and triethylamine (1.0 g) in ethanol (10 ml) gave a red solution from which water precipitated 4-benzyl-2-methylphthalazin-1(2*H*)-one (5) (1.04 g, 83%), m.p. 146–147.5° (from methanol) (lit.,⁴ 148°), ν_{\max} 1645 and 1590 cm⁻¹, τ (CDCl₃) 2.31–2.8 (m, Ar), 5.74 (s, CH₂), and 6.15 (s, NMe), identified by direct comparison with an authentic⁴ sample.

(c) The salt (3a) (1.75 g) was added to a solution of phenylhydrazine (2.27 g, 2.1 mol. equiv.) and triethylamine (2.2 g) in ethanol (30 ml). The mixture was heated under reflux for 20 min, then cooled, and the precipitated 4-benzyl-1,2-dihydro-2-phenyl-1-phenylhydrazonophthalazine (6) (2.53 g, 63%) was collected. It formed orange-yellow needles (from acetonitrile), m.p. 156.5–157.5°, ν_{\max} 3360w and 1600 cm⁻¹, τ (CDCl₃) 1.78–3.27 (m, Ar), 3.64br (disappears on addition of D₂O, s, NH), and 5.83 (s, CH₂) (Found: C, 80.2; H, 5.6; N, 14.1. C₂₇H₂₂N₄ requires C, 80.55; H, 5.5; N, 13.9%). Use of an equimolecular amount of phenylhydrazine resulted in a lower yield of compound (6).

Reaction of the Perchlorate (3a) with Amines and Ammonia.—(a) A solution of the salt (3a) (1.75 g) and benzylamine (1.07 g, 2 mol. equiv.) in acetic acid (20 ml) was boiled under reflux for 20 min. The resulting 2-benzyl-3-benzylamino-1-benzylidene-1*H*-isoindolium perchlorate (9) (2.22 g, 89%) crystallised from acetonitrile as pale yellow plates, m.p. 248.5° (decomp.), ν_{\max} 3210, 3130, 1650, and 1110br cm⁻¹ (Found: C, 69.6; H, 4.9; N, 5.45. C₂₉H₂₅ClN₂O₄ requires C, 69.5; H, 5.05; N, 5.6%). Deprotonation with aqueous sodium carbonate gave yellow 2-benzyl-1-benzylidene-3-benzyliminoisoindoline (10), m.p. 113–114° (from benzene-light petroleum), ν_{\max} 1640 and 1630 cm⁻¹, τ (CDCl₃) 2.0–2.9 (m, Ar), 3.95 (s, =CH), and 4.76 (s, 2 × NCH₂) (Found: C, 86.9; H, 6.0; N, 7.2. C₂₉H₂₄N₂ requires C, 86.95; H, 6.05; N, 7.0%).

(b) The red solution obtained by boiling a mixture of the perchlorate (3a) (1.75 g), benzylamine (1.2 g), and ethanol

¹² S. F. Nelsen and P. J. Hintz, *J. Amer. Chem. Soc.*, 1969, **91**, 6190.

¹³ E. D. Bergmann and A. Y. Meyer, *Israel J. Chem.*, 1969, **7**, 165.

(20 ml) for 30 min deposited orange-red 3-benzylamino-2-phenylindan-1-one (11a) (1.45 g, 93%) on cooling; m.p. 200—201° (from ethanol) (lit.,⁵ 198—199°), ν_{\max} 3320, 1662, and 1612 cm^{-1} , identical with an authentic sample prepared⁵ from benzylamine and 2-phenylindane-1,3-dione.

(c) A mixture of the perchlorate (3a) (1.75 g), aqueous ammonia (d 0.88; 20 ml), and ethanol (20 ml) was boiled for 3 min, cooled, and treated with water (20 ml). The resulting solid was filtered off and extracted with boiling ethanol (30 ml). The extract deposited red 3-amino-2-phenylindan-1-one (11b) (0.3 g, 27%), m.p. 261—263° (lit.,⁶ 260°; lit.,⁷ 278—280°); its i.r. spectrum was as reported.⁷

(d) The solution obtained by boiling a mixture of the salt (3a) (1.75 g), aniline (0.93 g), triethylamine (0.7 g), and ethanol (20 ml) for 30 min was cooled and water was added to incipient turbidity; the resulting orange-red 3-anilino-2-phenylindan-1-one (11c) (0.6 g, 40%) had m.p. 219—220° (lit.,⁶ 220—221°), ν_{\max} 3240, 1665, 1656sh, 1610, and 1600 cm^{-1} .

(e) The perchlorate (3a) (1.75 g) was added to ethanolic dimethylamine (5 ml), diluted with ethanol (7 ml). The mixture was boiled under reflux for 30 min, cooled, and treated with water. The precipitated 3-dimethylamino-2-phenylindan-1-one (11d) (1.03 g, 82.6%) crystallised from ethanol as red prismatic needles, m.p. 101—102°, ν_{\max} 1663, 1648, and 1596 cm^{-1} (Found: C, 81.6; H, 6.25; N, 5.65. $\text{C}_{17}\text{H}_{15}\text{NO}$ requires C, 81.9; H, 6.1; N, 5.6%). The indenone (11a) (1.15 g, 92%) was also obtained by adding the perchlorate (3a) (1.75 g) to a solution of triethylamine (1.4 g) in methanol (15 ml), keeping the resulting solution overnight, and then adding water.

Ethyl Cyano-(3-oxo-2-phenylindan-1-ylidene)acetate (14).—The perchlorate (3a) (17.5 g) was added to a solution of ethyl cyanoacetate (6.2 g, 1.1 mol. equiv.) and triethylamine (15.2 g, 3 mol. equiv.) in acetonitrile (100 ml). The resulting mauve solution was set aside overnight and then diluted with water (500 ml). Addition of concentrated hydrochloric acid precipitated the *ester* (14) (11.3 g, 71.4%), m.p. 132—133° (from benzene—light petroleum), ν_{\max} 2210, 1721, and 1608 cm^{-1} , ν_{\max} (CHCl_3) 2211, 1730, and 1615 cm^{-1} , τ (CDCl_3) 1.0—3.02 (m, Ar), 4.77 (s, $\geq\text{CH}$), 5.9 (q, CH_2), and 8.85 (t, Me), $\lambda_{\text{inf.}}$ * 251 (ϵ 14,000), 260 (12,600), and 332 nm (6500), $\lambda_{\text{max.}}$ * 300 nm (16,800) (Found: C, 75.6; H, 4.7; N, 4.35. $\text{C}_{20}\text{H}_{15}\text{NO}_3$ requires C, 75.7; H, 4.8; N, 4.4%). The orange 2,4-dinitrophenylhydrazone had m.p. 224.5—225° (from acetonitrile), ν_{\max} 3300, 2210, 1725, and 1618 cm^{-1} (Found: C, 62.9; H, 3.85; N, 14.3. $\text{C}_{26}\text{H}_{19}\text{N}_5\text{O}_6$ requires C, 62.8; H, 3.85; N, 14.1%). The *ester* (14) dissolved in aqueous sodium hydroxide, aqueous ammonia, or aqueous amines to give a bluish purple solution [$\lambda_{\text{max.}}$ 540 nm (ϵ 7100)] and was reprecipitated on acidification.

Cyano-(3-oxo-2-phenylindan-1-ylidene)acetamide (18).—On adding the perchlorate (3a) (3.5 g) to a solution of cyanoacetamide (1.68 g) and triethylamine (4.0 g) in acetonitrile (50 ml) a yellow solid formed which gradually dissolved during 12 h. Addition of dilute hydrochloric acid to the resulting purple solution precipitated the yellow *product* (18) (1.14 g, 39.5%), m.p. 339° (decomp., with previous darkening) (from acetonitrile), ν_{\max} 3430, 3316, 3180, 2208, 1734 (ketone), 1697 (amide I), 1647 (amide II), and 1602 cm^{-1} , $\lambda_{\text{inf.}}$ * 252 (ϵ 10,900), 261 (9400), and 330 nm (2600), $\lambda_{\text{max.}}$ * 298 nm (10,300) (the yellow colour is due to tailing into the visible region) (Found: C, 74.6; H, 4.2; N, 9.6.

* A trace of hydrochloric acid had to be added to prevent deprotonation.

$\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_2$ requires C, 75.0; H, 4.2; N, 9.7%). Its solution in aqueous ethanolic sodium hydroxide had $\lambda_{\text{max.}}$ 540 nm (ϵ 7800).

N-(3-Benzylidenephthalan-1-ylidene)morpholinium Perchlorate (3b).—A suspension of the morpholide (1b) (21.6 g) in acetic anhydride (75 ml) was slowly treated with perchloric acid (10 ml), with the temperature kept below 70°. Ether was added to the resulting solution and the precipitated semisolid material was washed three times with ether by decantation and then heated under reflux in acetic acid (120 ml) for 30 min; the *salt* (3b) (16.0 g, 58.4%) then separated. It crystallised from acetonitrile in pale yellow needles, m.p. 276—277° (decomp.), ν_{\max} 1670, 1609, and 1080 cm^{-1} (Found: C, 58.5; H, 4.7; N, 3.55. $\text{C}_{19}\text{H}_{13}\text{ClNO}_6$ requires C, 58.25; H, 4.65; N, 3.6%). The *salt* (3b) (1.3 g) was converted into 1-benzyl-4-morpholinophthalazine (4b) (0.99 g, 97%), m.p. 138.5—139° (from aqueous ethanol), ν_{\max} 1600 and 1110 cm^{-1} (Found: C, 74.4; H, 6.25; N, 13.5. $\text{C}_{19}\text{H}_{19}\text{N}_3\text{O}$ requires C, 74.7; H, 6.3; N, 13.75%) by treatment with a solution of hydrazine hydrate (0.25 g) and triethylamine (0.5 g) in ethanol (4 ml).

o-Isobutyryl-NN-dimethylbenzamide (22a).—A mixture of 3-isopropylidene-phthalide¹⁴ (60.7 g) and ethanolic dimethylamine (140 ml) was boiled under reflux for 1 h; removal of the solvent left the *amide* (22a) (76.4 g, 100%), m.p. 57.5—58.5°. The analytical sample had m.p. 58—58.5° (from light petroleum, b.p. 60—80°), ν_{\max} 1689 and 1630 cm^{-1} (Found: C, 71.0; H, 8.0; N, 6.25. $\text{C}_{13}\text{H}_{17}\text{NO}_2$ requires C, 71.2; H, 7.85; N, 6.4%).

(3-Acetoxy-3-isopropylphthalan-1-ylidene)dimethylammonium Perchlorate (23).—Perchloric acid (12.5 ml) was slowly added at temperatures below 70° to a solution of the foregoing *amide* (22a) (21.9 g) in acetic anhydride (80 ml). The *product* (23) (35.3 g, 97.8%) crystallised on cooling; m.p. 263—264° (decomp.), ν_{\max} 1780, 1688, 1608, and 1088 cm^{-1} , τ ($\text{CF}_3\text{CO}_2\text{H}$) 1.68—2.35 (m, Ar), 6.01 (s, NMe), 6.28 (s, NMe), 7.35br (q, J 6 Hz, CH), 7.67 (s, CO-Me), 8.7 (d, J 6 Hz, CMe), and 9.02 (d, J 6 Hz, CMe) (Found: C, 50.05; H, 5.55; N, 4.15. $\text{C}_{15}\text{H}_{20}\text{ClNO}_7$ requires C, 49.8; H, 5.6; N, 3.85%).

1-Isopropyl-4-dimethylaminophthalazine (24).—The foregoing perchlorate (23) (3.62 g) was added to a solution of hydrazine hydrate (1.0 g) and triethylamine (3.0 g) in ethanol (20 ml); after 20 min the mixture was diluted with much water, giving the *phthalazine* (24) (0.85 g, 39.4%), m.p. 62—63° (from light petroleum), ν_{\max} 1610 cm^{-1} (Found: C, 72.5; H, 8.1; N, 19.5. $\text{C}_{13}\text{H}_{17}\text{N}_3$ requires C, 72.5; H, 7.95; N, 19.5%).

(3-Isopropylidene-phthalan-1-ylidene)dimethylammonium Perchlorate (25a).—A solution of the acetoxy-compound (23) (10.66 g) in acetic acid (80 ml) was heated under reflux for 1 h and then allowed to cool, whereupon the *perchlorate* (25a) (4.0 g, 49.3%) separated; m.p. 274° (decomp.) (from acetic acid), ν_{\max} 1675, 1600, and 1090 cm^{-1} , τ ($\text{CF}_3\text{CO}_2\text{H}$) 1.68—2.4 (m, Ar), 6.08 (s, NMe), 6.26 (s, NMe), 7.59 (s, CMe), and 7.64 (s, CMe) (Found: 51.3; H, 5.6; N, 4.6. $\text{C}_{13}\text{H}_{16}\text{ClNO}_5$ requires C, 51.75; H, 5.35; N, 4.65%). Elimination of acetic acid, accompanied by much decomposition, also occurred when the *salt* (23) was briefly boiled in acetic anhydride. The perchlorate (25a) was recovered quantitatively after being heated with *p*-dimethylaminobenzaldehyde in acetic acid or acetonitrile for 3 h and after treatment with an acetonitrile solution containing molar equivalents of *N*-phenylmaleimide (or

¹⁴ A. Tasman, *Rec. Trav. chim.*, 1927, **46**, 653.

dimethyl acetylenedicarboxylate) and 1,8-bis(dimethylamino)naphthalene for 24 h.

Ethyl Cyano-(3-isopropylidene)phthalan-1-ylidene)acetate (28a).—The solution obtained by refluxing a mixture of the isopropylidene salt (25a) (1.5 g), ethyl cyanoacetate (1.13 g), triethylamine (1.5 g), and ethanol (50 ml) for 10 min deposited the *product* (28a) (1.1 g, 81.8%), as yellow needles (from ethanol), m.p. 178—179°, ν_{\max} (CHCl₃) 2210, 1712, and 1585 cm⁻¹, τ (CDCl₃) 1.43—2.77 (m, Ar), 5.72 (q) and 8.61 (t) (Et), and 7.71 (s, 2 × =CMe), τ (C₆H₆) 5.9 (q) and 8.93 (t) (Et), 8.02 (s, =CMe), and 8.44 (s, =CMe), λ_{\max} 266 (ϵ 19,800), 277 (18,400), 302 (5800), 315 (6900), 332 (6600), and 372 nm (13,200), λ_{infl} 390 nm (8900) (Found: C, 71.5; H, 5.7; N, 5.2. C₁₆H₁₅NO₃ requires C, 71.35; H, 5.65; N, 5.2%). The ester (28a) was obtained in only 22% yield when the condensation was conducted in acetonitrile solution. It was recovered after prolonged treatment with a solution of 2,4-dinitrophenylhydrazine in boiling aqueous methanolic sulphuric acid.

NN-Dimethyl-o-(diphenylacetyl)benzamide (22b).—This *amide* (15.7 g, 90.3%), m.p. 139—140° (from benzene-light petroleum), ν_{\max} 1695 and 1633 cm⁻¹ (Found: C, 80.1; H, 6.3; N, 4.0. C₂₃H₂₁NO₂ requires C, 80.4; H, 6.2; N, 4.1%) was prepared by adding ethanolic dimethylamine (75 ml) to 3-(diphenylmethylene)phthalide¹⁵ (15.1 g), diluting the mixture with ethanol (75 ml), heating on a steam-bath for 5 min, and then adding water.

NN-Dimethyl-(3-diphenylmethylenephthalan-1-ylidene)am-

monium Perchlorate (25b).—A suspension of the foregoing *amide* (22b) (10.4 g) in acetic anhydride (45 ml) was treated with perchloric acid (4.5 ml) in the usual way. The resulting solution was cooled and ether was added. The precipitated red oil was dissolved in acetic acid (20 ml) and the solution was heated on a steam-bath for 1 h. Addition of ether gave an oil which solidified during 2 weeks to yield the *product* (25b) (5.6 g, 43.8%) as yellow needles (from acetonitrile-ether), m.p. 124—126° (decomp.), ν_{\max} 1696, 1610, and 1090br cm⁻¹, τ (CF₃·CO₂H) 1.72—2.75 (m, Ar), 6.0 (d, NMe), and 6.22 (d, NMe) (Found: C, 64.7; H, 4.65; N, 3.25. C₂₃H₂₀ClNO₅ requires C, 64.85; H, 4.75; N, 3.3%).

Reaction of Perchlorate (25b) with Ethyl Cyanoacetate.—The foregoing perchlorate (25b) (2.13 g) was added to a solution of the ester (1.13 g) and triethylamine (1.5 g) in ethanol (30 ml). The mixture was boiled for 5 min, then cooled, and the bright yellow *ethyl cyano-(3-diphenylmethylenephthalan-1-ylidene)acetate* (28b) (1.0 g, 51.2%) was collected, m.p. 170—170.5° (from benzene-light petroleum), ν_{\max} (CHCl₃) 2210, 1720, and 1585 cm⁻¹, λ_{\max} 288 (ϵ 26,400), 299 (26,400), and 402 nm (22,900), λ_{infl} 267 (14,300) and 345 nm (9000) (Found: C, 79.5; H, 4.85; N, 3.6. C₂₆H₁₉NO₃ requires C, 79.35; H, 4.9; N, 3.55%).

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¹⁵ T. W. Koenig and J. C. Martin, *J. Org. Chem.*, 1964, **29**, 1520.